Effect of step structure on ordering in GaInP

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$Ga_{0.5}In_{0.5}P$ layers grown by organometallic vapor phase epitaxy at rates of between 0.1 and 4.0 μm/h on exactly (001)-oriented GaAs substrates have been studied using atomic force microscopy. The surface is found to be covered by islands several monolayers in height that are elongated in the [110] direction. The edges of the islands are formed of clearly resolved bilayer (5.9 Å) steps. Monolayer steps are rare and no steps larger than 6 Å were observed. These observations explain the nature of the order twin boundaries in ordered GaInP grown on exactly (001)-oriented substrates. The (001) domain laminae are always found to consist of an even number of monolayers. For bilayer steps, the domain thickness will be twice the number of steps moving across the surface before the direction of step motion switches due to the undulating nature of the surface. This switch in the direction of step motion at a particular location on the surface produces the order twin boundaries observed. © *1995 American Institute of Physics.*

Cu–Pt ordering, a segregation of atoms into alternating (111) layers during vapor phase epitaxial growth, is observed in essentially all III/V alloys.[1] Attempts to understand the atomic scale mechanism leading to ordering are important from a fundamental viewpoint. In addition, Cu–Pt ordering is of practical significance mainly because it is observed[2] to cause a marked decrease in the band-gap energy of GaInP, with similar effects predicted for other alloys.[3]

The occurrence of Cu–Pt ordering is widely accepted to be entirely due to surface processes. This structure is thought to be stable only at the (2×4) reconstructed (001) surface.[4] Models advanced to explain the mechanism by which the ordered structure is formed generally postulate the orderly advance of monolayer [110] steps across the surface.[1,4,5] However, for GaInP grown by organometallic vapor phase epitaxy (OMVPE), where the highest degree of order is observed, neither the reconstruction nor the nature of the surface steps had, until recently, been observed experimentally. The optical technique of surface photoabsorption has been used to probe the (001) surface of GaInP during OMVPE growth. The results indicate the presence of P dimers on the surface with a $[\bar{1}10]$ orientation consistent with formation of the (2×4) reconstruction.[6]

Reports have also recently appeared of scanning tunneling microscopy (STM) and atomic force microscopy (AFM) studies exploring the physical nature of the steps on the GaInP surface during OMVPE growth. Several groups have reported monolayer steps on epitaxial GaAs surfaces.[7–9] Kasu and Kobayashi[8] STM study the two-dimensional islands formed on exactly (001)-oriented GaAs substrates during OMVPE growth of GaAs at a rate of 0.17 μm/h, a V/III ratio of 200, and temperatures of 530, 580, and 650 °C. The islands were observed to be elongated in the [110] direction, orthogonal to the direction of elongation for islands formed during molecular beam epitaxial (MBE) growth of GaAs.[9] They were found to be delineated largely by a combination of [110] and $[\bar{1}10]$ oriented monolayer (2.9 Å) steps. Some step bunching was observed at 580 °C, but even there, monolayer steps were observed. Interestingly, the island shapes are similar to those observed for macroscopic islands formed on photolighographically patterned GaAs substrates after OMVPE growth for high arsine partial pressures by Asai.[10] The difference between MBE and OMVPE islands could be ascribed, in the model of Asai, to the vastly different As partial pressures at the interface in OMVPE and MBE. Kasu and Kobayashi[8] attribute the difference to a difference in adatom attachment kinetics at the step edges, which might be due to the different atomic configurations at the $[\bar{1}10]$ steps for OMVPE and MBE described here.

This letter is concerned with the steps and islands, observed using AFM techniques, formed on the surface of $Ga_{0.5}In_{0.5}P$ layers grown by OMVPE on exactly (001)-oriented GaAs substrates. The results are used to further our understanding of the ordering mechanism as well as the order twin boundaries observed in the epitaxial GaInP layers.

The $Ga_{0.52}In_{0.48}P$ layers described in this study were grown by OMVPE at 670 °C in a horizontal, infrared-heated, atmospheric-pressure reactor.[11,12] The sources were trimethyl-indium and -gallium combined with the group V hydrides. The growth rate was varied from 0.1 to 4.0 μm/h, keeping the input V/III ratio between 160 and 220 except for the layer grown at 0.1 μm/h where the V/III ratio was 2000. A thin (0.15 μm) GaAs buffer layer was grown before initiating growth of the GaInP layer. The GaInP layers were $\sim$1 μm thick, except for the layer grown at 0.1 μm/h, where the thickness was 0.4 μm.

The surface structure was characterized using a nanoscope III AFM in the tapping mode. Etched single-crytstalline Si tips were used with an end radius of about 5 nm and a sidewall angle of about 35°. Scan rates of 1–2 lines per second were used and data were taken at 512 points/line and 512 lines per scan area. This technique has been demonstrated to allow imaging of features one atomic layer in height.[7,13]

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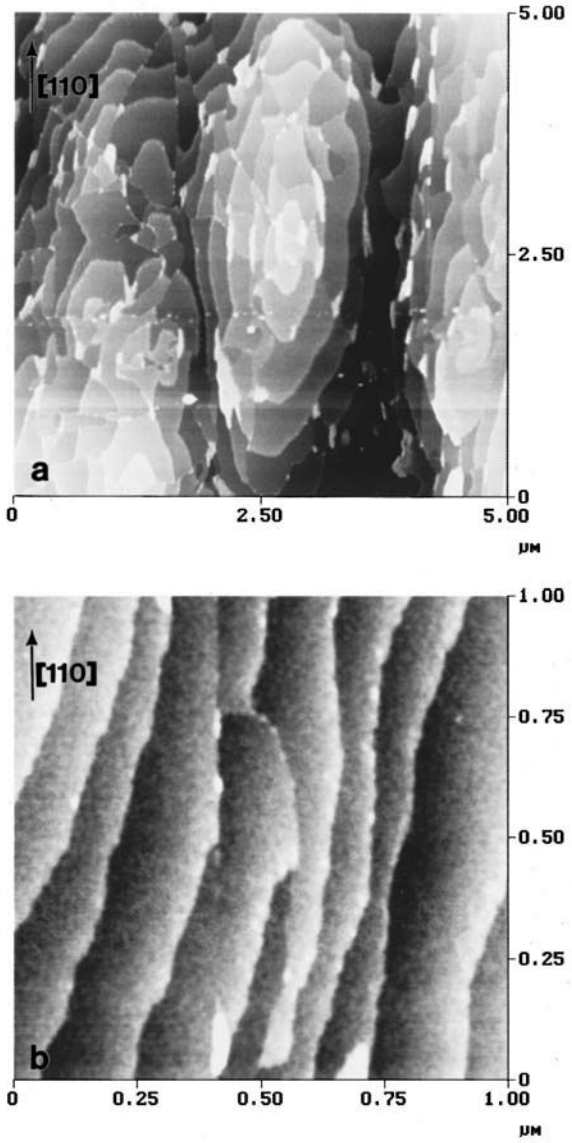

FIG. 1. Atomic force microscopic images of the surface of a GaInP layer grown at 670 °C at a rate of 0.1 μm/h lattice matched to a GaAs substrate having the exact (001) orientation: (a) low magnification in the *x*-*y* plane and (b) higher magnification.

The surface of the $Ga_{0.5}In_{0.5}P$ layer grown at 0.1 μm/h shows well-defined islands of up to 60 Å in height. As seen in Fig. 1(a), the islands are elongated in the [110] direction, similar to the islands observed on GaAs layers grown by OMVPE on (001) GaAs substrates.[8] The sides of the islands are seen to be made up of large terraces terminated by steps. Figure 1(b) is a higher magnification view of the nearly [110] steps at the edge of the island. As seen in Fig. 2, a scan showing the surface topography of this region of the surface, the steps have an average height of 5.9 Å; thus, they are bilayer steps. Monolayer steps can occasionally be found, as seen in Figs. 1(b) and 2, but no bunching to produce larger steps was observed. The angles between the (001) surface and the edges of the islands are very small (much less than 1°). This contrasts with reports of the spontaneous formation of facets during growth of very thick (>10 μm) GaInP layers on exactly (001)-oriented GaAs substrates,[14] where the [110] facets are oriented at an angle of ~4° with the (001) surface.

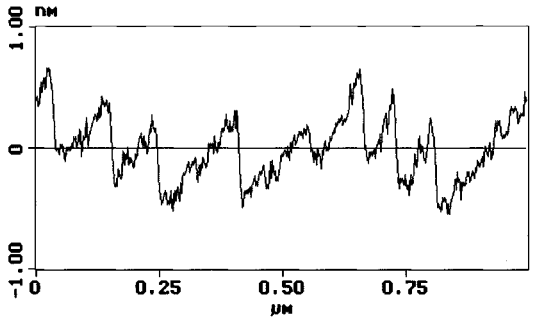

FIG. 2. Atomic-scale profile of the surface of the GaInP sample shown in Fig. 1(b) showing the presence of bilayer steps ~5.9 Å high.

The island and step structures are approximately the same for the layers grown at other rates of 0.5, 1.0, 2.0, and 4.0 μm/h. The reason for the formation of bilayer steps is unclear. However, it seems unlikely that any kinetic mechanism could explain such uniform steps. More likely is a thermodynamic explanation based on reconstruction at the step edges. Single steps will always form a row of dangling P bonds.

The step spacing is ~1250 Å for the layer grown at 0.1 μm/h and decreases with increasing growth rate as seen in Fig. 3. The trend is the same as for (001) facets formed due to step bunching on GaInP layers grown on vicinal (001) substrates with misorientation by angles of 3°–9° to produce [110] steps on the surface.[15] The (001) facet lengths appear to be approximately a factor of 2 smaller than the bilayer step spacings observed here. Both may be controlled by the adatom diffusion lengths, which would account for the nearly equal values and give the $1/(\text{growth rate})^{1/2}$ dependence observed.

The bilayer step structure observed leads to an explanation for the defects observed in ordered GaInP layers grown by OMVPE on exactly (001)-oriented GaAs substrates. Baxter *et al.*[16] describe the extremely complex structures formed, consisting of two variants of the Cu–Pt structure with ordering on the $(\bar{1}11)$ and $(1\bar{1}1)$ planes distributed in alternating (001)-oriented laminae. Although the lamina thicknesses vary, each invariably consists of an even number of atomic layers. The results presented here suggest that this is accounted for by the motion of bilayer steps across the surface. A sequence of *n* steps will produce a lamina of thickness

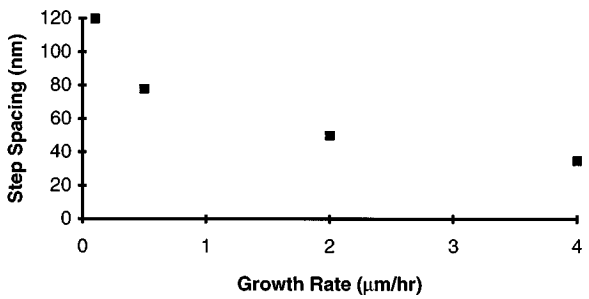

FIG. 3. Bilayer step separation vs growth rate for GaInP samples grown at 670 °C lattice matched to exactly (001)-oriented GaAs substrates.

2n/(ML), where ML is the thickness of a single monolayer, 2.8 Å in this case. The following lamina of the other variant must be due to a series of steps moving in the opposite direction.[17] This would be expected due to the undulating nature of the surface consisting of islands which shift in both size and position as growth proceeds.

A number of models have been postulated to explain the ordering mechanism.[1,4,5] Most agree that formation of the two variants of the Cu–Pt ordered structure observed requires the surface to have the (2×4) reconstruction consisting of $[110]$ oriented group V dimer rows. The interaction of $[110]$ steps with the dimer rows appears to be a key feature of the ordering mechanism. The $[110]$ steps are typically considered to be one monolayer in height. The model of Stringfellow and co-workers[4,17] gives a plausible mechanism for the formation of the two B variants of the Cu–Pt structure in a material with mixing on the group V sublattice, such as GaAsP, based on the different attachment energies of group V adatoms at the two types of steps, one where the surface group V atom has formed a dimer bond with its neighbor, and one where it has not. The positions of the dimer bonds on the (2×4) reconstructed surface are determined by the sizes of the underlying group V atom in the second layer beneath the surface.

Ordering in an alloy with mixing on the group III sublattice, such as GaInP, is postulated to be due to a similar mechanism. The group III atoms are aligned into alternating In- and Ga-rich $[110]$ rows due to a reduction in the local strain energy.[18] The information about the positions of the group III atoms in the third layer beneath the surface is conveyed to the surface (the phase-locking mechanism) as an alternating tensile and compressive strain in the surface P atoms.[19] This determines the positions of the P dimers: they form where the P atoms are closest together.

This model is very similar to that postulated for the formation of $\{111\}$ ordered structures in Ge–Si alloys by LeGoues *et al.*,[20] who suggest that the atoms diffuse in the subsurface layer to the lowest energy positions, i.e., with the larger Ge atoms in the sites between dimer rows and the smaller Si atoms in the compressively strained sites directly beneath the dimer rows. Similar calculations have been used to support the use of this model for the formation of several ordered structures in GaInP.[21]

The only distinction between the two models described above is that the former model[4,17] involves only surface processes while the latter mode[20,21] requires subsurface diffusion of the Ga and In atoms. This seems unlikely for the third layer of atoms given the short time (<1 s) allowed for the diffusion to take place and the extremely slow diffusion coefficients for III/V alloys at these temperatures. The diffusion would clearly not be rapid enough if bulk diffusion coefficients are applicable.

Either model can be used to explain the ordering even when the surface is covered with bilayer steps. In this case, the chemical selectivity of the first model comes from the bonding of the group III atoms at the bottom of the riser. It is postulated that one type of group III atom will prefer to insert itself into the P–P dimer bond on the (2×4) surface at the bottom of the step edge while the other will selectively incorporate where no P–P dimer bond is broken.

In summary, atomic force microscopic examination of the surfaces of GaInP layers grown by OMVPE lattice matched to exactly (001)-oriented GaAs substrates reveals three-dimensional islands several monolayers in height. At the island edges bilayer steps, ~5.9 Å high, are clearly resolved. The GaInP spontaneously forms the Cu–Pt ordered structure during epitaxial growth. The complex nature of the ordered microstructure can be explained, in part, by the bilayer steps. Alternating (001) laminae of the $(\bar{1}11)$ and $(1\bar{1}1)$ variants of the Cu–Pt structure are formed during growth. The laminae always consist of an even number of monolayers. This is due to the motion of the bilayer steps, which produce 2 ML of ordered material of a particular variant with each pass of the step in a particular direction. Of course, the number of steps passing a certain point on the surface determines the lamina thickness. The undulating nature of the surface is postulated to produce steps moving in the opposite direction at a later time, resulting in the formation of a lamina of the second variant separated from the first lamina by an order twin boundary.

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